Environmental Impact of Uranium Mining and Ore Processing in the Lagoa Real District, Bahia, Brazil[†]

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Uranium mining and processing at Lagoa Real (Bahia, Brazil) started in 2000. Hydrogeochemical monitoring carried out from 1999 to 2001 revealed generally good quality of the water resources outside and inside the mineralized area. No chemical contamination in waters for domestic uses was observed. Hydrochemical characteristics did not vary significantly after 1 year of U exploitation, as compared to premining conditions. Due to the short time of mining, the results cannot exclude future variations in water quality. Leaching experiments helped to describe processes of ore and waste degradation. Sulfate was identified as an indicator for different types of contamination. Potential hazards related to local climate (hot rainy season) were identified. They indicate that tailings derived from the ore processing, destabilized by sulfuric acid attack, may induce acidification and salinization in the surrounding environment. Another potential source of environmental impact could be linked to local radium-rich mineralization, originating radon emission.

Introduction

Toxicity and radioactivity of uranium are the main environmental concerns for exploitation and processing of U-ore. In areas where U mining is planned, a careful assessment of toxic and radioactive element concentrations is recommended, before mine activity starts, to evaluate the background of harmful elements and to prevent future contamination. Inhalation and ingestion with food or drinking water are the most common forms of U penetration into the human body (*1*). Depending on the solubility of the inhaled compound, U may remain some time in the lung and then will be transferred into the blood, conversely to ingested U,

from which only <2% will reach the blood and the rest is eliminated. From U dissolved in the blood, the bones fix strongly some 20%, the kidneys another 15%, and the rest is eliminated with urine. Uranium may induce cancer in lung and bone because of its α and β radioactivity; in kidney the main concern is its chemical toxicity, like other heavy metals.

In this study, key parameters for the evaluation of water quality were monitored before and 1 year after U mining and processing facility operation near Lagoa Real in the state of Bahia, Brazil. This work was aimed at assessing the chemical quality of water resources at a district scale in order to (a) identify possible vertical and lateral migration of toxic metals from the mineralized areas in the hydrological system, (b) characterize solid waste materials susceptible to affecting the mobility of toxic elements, and (c) identify weathering processes and potential dispersion paths.

Studied Area

Site Description. The Lagoa Real U-District extends 1200 km² and is limited by the 42° 09′−42° 23′ W and 13° 45′−14° 07′ S geographical coordinates. The district hosts about 60 000 people, partially in small or large villages (up to 12 000 inhabitants) or scattered over the country. Main economic activities comprise poorly developed farming and cattle breeding; main products are maize, beans, cotton, cassava, sugar cane, milk, eggs, and honey. The climate is semiarid tropical with mean precipitation of 800 mm/year. Seasonal precipitation ranges from a few millimeters (June−August) to nearly 700 mm (November−January). Mean temperatures in the year vary from 14 to 29 °C, and the relative air humidity varies from 60% to 74%. Elevation ranges from 900 to 1050 m above sea level in the western part to 500−650 m in the eastern part. The area is dusty and covered with rare vegetation; the soil is sandy-lateritic (immature latosoil). Typical vegetation consists of small palm trees, shrubby trees, prickly plants and many species of Cactaceae. The surface drainage is controlled by two fault systems, which strike on north 220° and north 320° directions, and is marked by intermittent streamlets. The only perennial stream is the river Sao Joao flowing eastwards in the southern border of the district.

Geological Frame, Uranium Mineralization, and Mining. The geological frame of Lagoa Real (Figure 1) comprises the Archaean gneiss migmatite complex (GMC) that flanks the Proterozoic N−S trending Lagoa Real complex (LRC). The GMC is made up of high-grade metamorphic rocks of granodiorite and quartz−monzonite composition. The LRC comprises three evolutionary stages: (a) formation of granite adamellite rocks metamorphosed from 2.9 to 2.6 Ga to form migmatite gneiss; (b) intrusion of granite from 1.75 to 1.50 Ga; and (c) intense tectonic−metamorphic processes that led to augen, band-crenulated and mylonitic gneiss of 0.7−0.5 Ga, and associated albitites (*2*, *3*). The dominant rocks belong to stages b and c.

Albitites in lenslike bodies were formed by the action of hydrothermal solutions responsible for the sodium metasomatism (oligoclase and microcline replacement by albite) and the deposition of U-oxide (*2*). Their mineral composition is albite (≥70%) with quartz (traces to 15%), magnetite (traces to 15%), aegirina−augite (traces to 10%), garnet (traces to 10%), and microcline (traces to 5%). Allanite, epidote, sphene, zircon, and uraninite, and occasionally calcite, fluorspar, and apatite, are accessory minerals.

The first record of U mineralization was achieved in July 1977. Later on, a prospecting program carried out by Empresas Nucleares Brasileiras (NUCLEBRAS) has confirmed
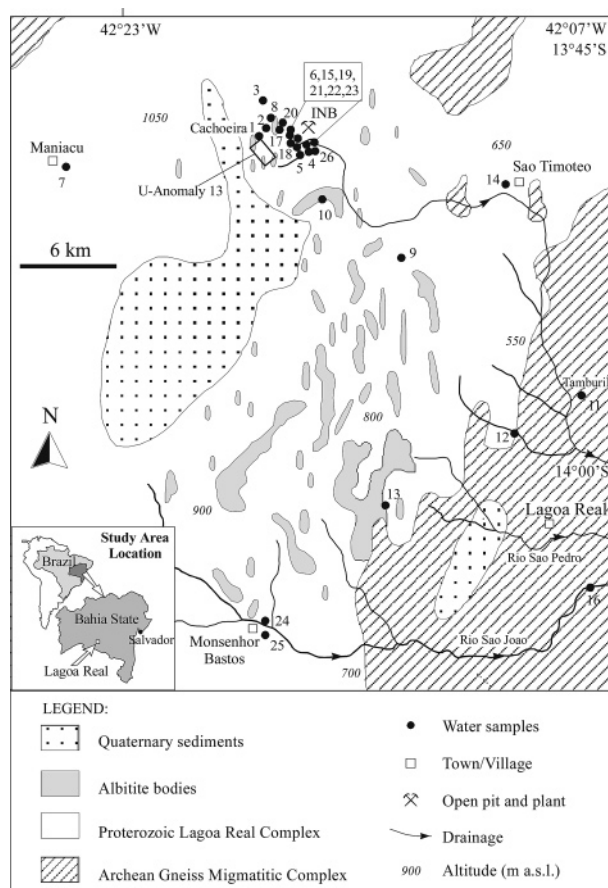
FIGURE 1. Simplified geological map of the Lagoa Real U-district showing the location of water samples. The small map shows the location of the study area in Brazil.

the existence of several U-mineralized bodies hosted in the LRC albitites near Lagoa Real (4, 5). The U deposit comprises 34 occurrences distributed over a 30 km long and 10 km wide N−S belt. Uraninite is the main ore mineral; pitchblende and uranophane subordinately occur. The average ore grade is 0.18% U_3O_8. Total ore reserves are estimated at 90 000 000 tons with 0.03% U_3O_8 as cutoff grade.

In January 2000 the Industrias Nucleares do Brasil (INB, a Brazilian state company), built a plant to concentrate the U as ammonium diuranate. A scheme of the ore processing is shown in Figure 2. It comprises crushing and grinding, H_2SO_4 leaching in pile, solvent extraction by kerosene, and U precipitation by NH_4OH. When fully operating, the plant is expected to produce 478 tons/year U_3O_8; this quantity equals the domestic demand. The open-air leaching basin is made up of welded high-density polyethylene foils on a clay-based ground. The waste resulting from processing is accumulated in large basins where, at bottom, a 1 m thick clay layer has been spread as an impervious barrier to protect the environment.

Field and Laboratory Work

Water Sampling and Analysis. A first campaign was performed in May 1999 before the start of exploitation. Seventeen water samples were collected from drillholes (depth 40−100 m), wells (depth 3−10 m), ponds, and streams. In September 2000, 16 water samples were collected and included seven drillholes already sampled, new drillholes, shallow groundwater (well depth 5 m), and deep wells that supply water to large villages. In February 2001, 15 out of 16 water samples were collected from places previously sampled. A total of 26 waters were investigated (10 were sampled twice, and six,
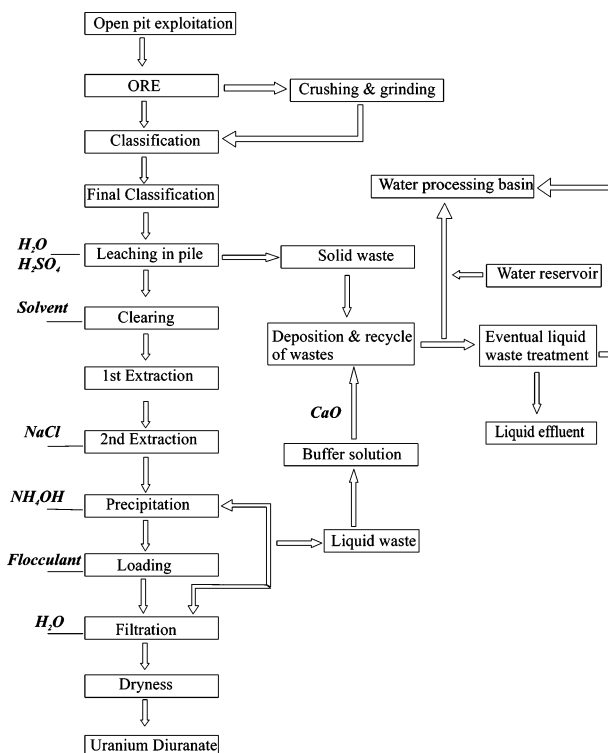

FIGURE 2. Flowchart of the uranium ore processing at Lagoa Real.

three times). The location of water samples is shown in Figure 1. Sample description is available in the Supporting Information.

In the field, temperature, pH, redox potential (Eh), conductivity, alkalinity, and dissolved oxygen (by Wissenschafttlich Werksatten GmbH devices) were measured; waters were filtered (0.45 μm unless otherwise specified) and stored in HNO_3-cleaned high-density polyethylene or polycarbonate flasks. Aliquots for cation analysis were acidified to pH < 2. Ion chromatography (IC, Dionex) was used for anion analysis, atomic absorption spectroscopy (AAS) (Perkin-Elmer 2100) and inductively coupled plasma optical emission spectroscopy (ICP-OES) (ARL-Fisons 3520) for major cations, and ICP-mass spectrometry (MS) (Perkin-Elmer Elan 5000) for trace elements. Deuterium and oxygen-18 in water were determined by mass spectrometry; values in delta notation are calculated versus the Vienna−standard mean ocean water (V-SMOW) reference.

Aqueous uranium in aliquots acidified to pH = 2 with HNO_3 was determined by different techniques. Total (unfiltered) and dissolved (filtered at 0.22 or 0.45 μm) U was analyzed by time-resolved laser spectrofluorometry (TRLS) with a Dilor and a Scintrex device, and by ICP-MS (PQ ExCell from VG Elemental and Perkin-Elmer Elan 5000). The most sensible reagent for U analyses by spectrophotometry was arsenazo III; this method requires the reduction of UO_2^{2+} (6, 7). The 2-(2-thiazolylazo)-p-cresol (TAC) method (8) showed to be useful for concentrations > 10 μg L^{-1} U.

At sites where the water was supposed to interact with the mineralization, 250 mL of water, filtered at 0.22 μm and acidified with HNO_3 to pH = 2, was collected for measuring $^{234}U/^{238}U$ disequilibrium by α-spectrometry (Camberra Alpha analyst system). Isotopic data, combined with total U, may provide information on the stability of U minerals in the ore.

Radiometric Survey. In October 1999, ^{222}Rn and ^{226}Ra dissolved in water, ^{222}Rn and ^{220}Rn in soil-trapped air (degassing unit EDA-RDU-200), and K, U, and Th in sediments by field γ-spectrometry (Geofyzika-512) were determined. Radium in water was determined by scintillometry

TABLE 1. Concentrations of Uranium, Radon-222, Radium-226, Oxygen-18, and Deuterium in Water Samples from the Lagoa Real U-District

no.	date (dd.mm.yy)	U^a (μg L^{-1}) a	b	c	d	e	f	g	^{222}Rn (pCi L^{-1})	^{226}Ra (pCi L^{-1})	‰ (V-SMOW) δ^{18}O	δ D
1	06.05.99	230		250	320	223	280	198	89923	7.1	−4.11	−21.8
	19.09.00			318	327	280	319	240		3.3		
	14.02.01		377			275		201				
2	07.05.99			6	7.4	6		5.7		0.9	−3.73	−24.7
3	07.05.99	<10			0.5	1.1		1		<0.1	−1.07	−5.8
4	07.05.99	<10		12.3	12.5	8.4	5.6	7.6	3817	0.6	−3.90	−24.8
	19.09.00			13.7	15.2	13	14.1	6				
	14.02.01		11.5			12		11.8				
5	07.05.99	<10		3.4	3.6	3	3.7	2.5	5322	<0.1	−3.90	−25.4
	19.09.00			7.5	9.5	7.6	8.4	6.7				
	14.02.01		8.11			6.3		4.8				
6	07.05.99	<10		9.3	9.8	8.2		7.6	2266	1.1	−3.87	−24.0
	19.09.00			14.2	10.9	10.2	11.4	8.3				
7	08.05.99	<10		1.3	1.5	1	1.34	1.1	26428	10.1	−4.66	−27.0
	20.09.00			3.1	2.7	1.55	1.57	1.1		11.7		
	14.02.01		<7			1.4		1.4				
8	08.05.99	<10		3	2.6	2.1		2.5		0.3	−3.82	−20.1
9	08.05.99	<10		0.16	0.2	0.2		0.2		0.5	−3.88	−24.7
	15.02.01		<7			0.45		0.5				
10	08.05.99	<10			0.12	0.2		0.2		<0.1	4.70	14.8
	15.02.01		<7			0.40		0.4				
11	09.05.99	<10		11.4	10.7	8.9		7.6		1.3	−4.17	−24.7
12	09.05.99	<10		0.43	0.41	0.5		0.5		0.1		
13	09.05.99	<10		0.14	0.15	0.1		0.1		<0.1	−1.28	−11.9
14	10.05.99	<10		1.85	1.75	1.4		1.6	3645	2.5	−4.07	−26.7
	20.09.00			3.7	3.6	1.94	2	1.5				
	15.02.01		<7			2.37		2.2				
15	10.05.99	354		500	720	260	464	238	3020	1.4	−4.10	−23.4
	19.09.00			46.7	31.5	30.5	34.8	25				
	14.02.01		30			31		33				
16	10.5.99	<10		0.3	0.45	0.8		0.7	1114	<0.1	−0.82	−12.0
17	18.09.00			7.6	8.2	7.5		7.6				
18	18.09.00			10.6	11.4	10	11	8.6				
	15.02.01		<7			2.3		2				
19	19.09.00			41.8	43.1	37.1	39.3	32				
	14.02.01		46			45.8		46				
20	18.09.00			3.2	2.8	1.44	1.42	1				
21	18.09.00			33	34.6	32	29.8	26				
	15.02.01		29			34		33				
22	18.09.00			7.4	7.4	6.3	6.8	5.2				
	15.02.01		12			5.3		5.7				
23	19.09.00			4.1	4.6	3.09	3.25	2.7				
	14.02.01		<7			7.6		6.7				
24	20.09.00			3.1	2.7	2.05	2	1.5		1.8		
	15.02.01		<7			2.5		2.2				
25	20.09.00			<DL	<DL	0.11	0.17	<0.1				
	15.02.01		<7			0.15		0.3				
26	14.02.01		46			47		49	2474			

^{a} (a) Filtered 0.45 μm, spectrophotometry (6). (b) Filtered 0.45 μm, Arsenazo method (7). (c) Filtered 0.22 μm. (d) Nonfiltered. (e) Filtered 0.45 μm, Elan ICP-MS. (f) Filtered 0.22 μm, smart ICP-MS. (g) Nonfiltered, Scintrex.

(modified Rashing Camberra) 30 days after the water collection. This is the required time for the decay of radon and the production of ^{222}Rn in equal amount to that of the remaining parent ^{226}Ra.

Leaching Experiments. Four solid samples (about 2 kg each) were collected randomly at the stockpile of tailings derived from the sulfuric acid processing: LRS1, LRS2, and LRS3 were used for batch experiments and LRS4 was used for flow-through reactor experiments. For flow-through reactor experiments, two solid samples were collected at the INB plant: LRS5 was sampled at the waste-rock deposit (U-poor material), and LRS6 is U-rich ore collected before the milling.

Batch experiments on 500 g of solid samples were carried out with 1500−2100 mL of deionized water at room temperature (25 °C). The solid sample and water were mixed in glass containers under continuous stirring. At defined intervals (1, 4, 7, 24, 48, and 72 h, and for the LRS3 sample till 192 h) the solution was extracted and it was replaced by a new amount of deionized water. An aliquot of each extracted solution was filtered (0.45 μm) and analyzed by ICP-MS.

For flow-through reactor experiments, solid samples were dried and sieved between 0.35 and 0.80 mm. Approximately 750 g of the selected grain size was introduced into a 2.4 cm inner diameter Pyrex column. Distilled and deionized water, saturated with 5% CO_2–95% air mixture, was introduced by a peristaltic pump (flow rate 10 mL/h) in a glass inlet fitted at the basis of the column. pH of the input solution was constant and equal to 4.2. At regular intervals, the output solution of each column was collected with a syringe and stored in Falcon tubes after pH measurement and filtration. Major cations were determined by AAS, anions by IC, silica by automatic colorimetry, and U by Scintrex TRLS.
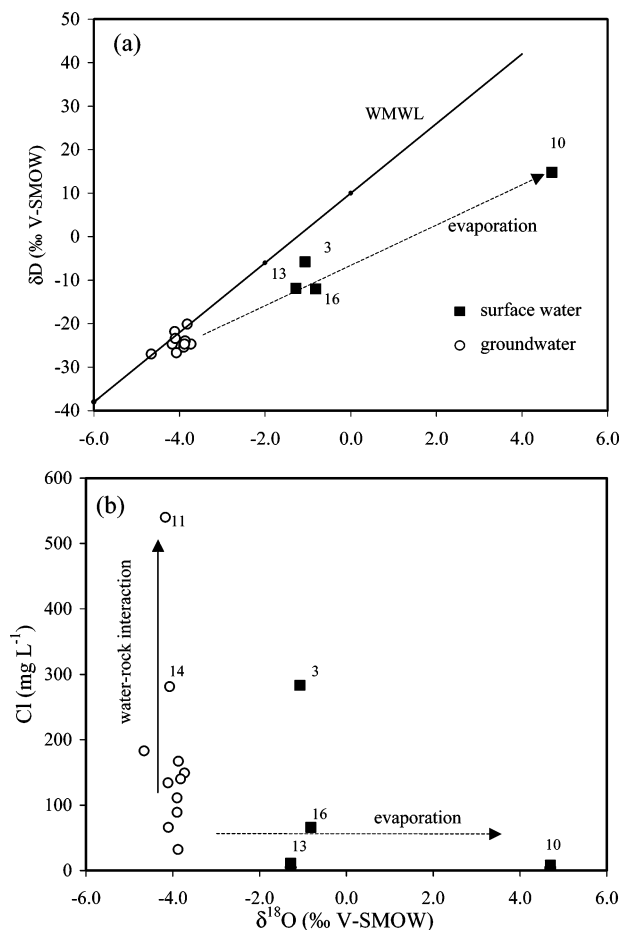
FIGURE 3. Deuterium (a) and dissolved chloride (b) versus oxygen-18 in waters at Lagoa Real (sampling in 1999). WMWL: world meteoric water line.

Results and Discussion

Hydrogeochemistry. Concentrations of major components and selected trace elements in waters collected at Lagoa Real are available in the Supporting Information. Concentrations of radioactive elements and stable isotopes are reported in Table 1. Preliminary results are reported in ref *9*. The complete data set can be found in ref *10*.

Water in the whole area is characterized by low salinity (generally <0.80 g L^{-1}), which indicates low weathering processes due to scarce infiltration and short circulation time in silicatic environments. Surface water is less saline and relatively enriched in bicarbonate and magnesium. pH of drillholes, wells, and springs is close to neutrality, while streams and ponds show pH values around 8. Dissolved oxygen corresponds to equilibrium with atmosphere for surface waters, while slightly reducing conditions occur in some drillholes. No significant seasonal change in major components occur: water sampled more than once shows quite homogeneous values, with the exception of sample 10, a semipermanent pond water where variations in dissolved oxygen and pH are likely related to biological activity.

δD and δ^{18}O results are plotted in Figure 3a. Groundwater samples form a cluster around the world meteoric water line. Surface water is significantly enriched due to evaporation; this is clearly observed in the pond sample 10, sampled after a dry period. The corresponding line has a slope of 4.5, consistent with usually found values for evaporation processes (*11*). Chloride concentrations versus δ^{18}O are plotted in Figure 3b. It shows that the evaporation process occurs in the less saline, surface waters.

The waters have predominantly Na−Ca−HCO$_3$−Cl composition with very low SO$_4$ (Piper diagram available in the Supporting Information). The dominant anion in surface waters varies according to the subjacent mineralogical context: chloride corresponds to the mineralized area and carbonate to the Lagoa Real complexes. The general chemistry of groundwater corresponds to weathering processes in the regional gneiss or gneiss hosting albitite context. In fact, Na/Cl shows a slight excess of sodium with respect to seawater (figure available in the Supporting Information), due to albitite dissolution. Those samples located outside the mineralized area in a granitic−migmatite environment do not show sodium enrichment.

Modeling with PHREEQC software (*12*) using the MINTEQ database shows that most drillhole waters are saturated with respect to calcite (figure available in the Supporting Information) and other carbonates (siderite, rhodocrosite). Silica concentration corresponds to saturation with a microcrystalline solid phase, probably opal, a common form in subsurface contexts. All this indicates that groundwaters are close to equilibrium with neogenic solid phases formed by weathering of the host rocks.

Uranium content is not significantly different in filtered and unfiltered samples, indicating that it is transported mostly in dissolved forms. Particulate U (20−30%) was detected only in samples showing the highest U concentrations (samples 1 and 15, located in the heart of the mineralized area). Particulate U was associated with high iron and/or manganese in colloidal forms, onto which uranium could be sorbed. In surface water, dissolved U is <1 μg L^{-1}. The groundwaters likely circulating in granitic rocks also show low dissolved U (<4 μg L^{-1}). On the contrary, in albitite areas dissolved U is much higher, in a large range, with some high values. Uranium in water appears to be clearly linked to albitites. The U-rich waters are saturated with uranophane Ca(UO$_2$)$_2$(SiO$_3$OH)$_2$·5H$_2$O, in agreement with the secondary mineralization observed in the area (*13*), but they are undersaturated with uraninite. The activity ratio ^{234}U/^{238}U, measured in samples with the highest U contents, is not significantly different from 1 and indicates a congruent dissolution of U isotopes from a homogeneous mineralization (*14*).

Two anomalous ^{222}Rn concentrations in water were recorded, both associated with the highest ^{226}Ra contents (samples 1 and 7). Since these samples show very different U concentrations, the existence of a radium accumulation process disconnected from the U mineralization is supposed. The high barium values observed in samples 1 and 7, corresponding to saturation with barite in both waters, suggest the presence of radiferous barium minerals at depth.

Radiometric Data. Table 2 reports the radiometric data of ^{222}Rn and ^{220}Rn in the air trapped in soil at sites distant from the mineralization (Maniaçu), near the mineralized area (Cachoeira), and in the mineralized body (U anomaly 13). In the ore outcrop, ^{222}Rn and ^{220}Rn concentrations in soil-trapped air show the highest values due to emanation. Radon values are lower near drillholes located outside the anomaly zones, whatever the U concentration in the water. This indicates that radon migration is to some extent independent from water flow and is mainly confined at the ore outcrop.

Uranium, thorium, and potassium contents measured in rock samples are available in the Supporting Information. Mean Th and U concentrations in nonmineralized areas are 19 and 3 ppm, respectively, and Th/U ratio is in the range of 3−10. These data are consistent with average ratios reported in granitic contexts (*11*). High values of U (up to 600 ppm) occur in outcropping mineralized albitites; the low Th/U ratio (0.15) observed in these cases is reasonably explained by the mineralizing process, characterized by

TABLE 2. Radiometric Data of ^{222}Rn and ^{220}Rn in the Air Trapped in Soil

	^{222}Rn		^{220}Rn		
locality	pCi L^{-1}	Bq L^{-1}	pCi L^{-1}	Bq L^{-1}	remarks
Maniaçu	830	31	4253	157	adjoining drillhole no. 7
Cachoeira PC-01 (a)	425	16	250	9	adjoining drillhole no. 1
Cachoeira PC-01 (b)	970	36	393	15	in the drainage valley
Cachoeira PC-01 (c)	1126	42	1569	58	in the slope
U anomaly 13 (a)	37 582	1392	1726	64	base of the slope
U anomaly 13 (b)	215 178	7970	nd[a]	nd	way up
U anomaly 13 (c)	72 485	2685	19 726	731	on top
U anomaly 13 (d)	80 613	2986	13 433	497	on top

[a] Not detected.

differential dissolution−precipitation mechanisms and preferential migration of the more soluble U.

Water Quality. The data collected at Lagoa Real indicate good quality of groundwater and surface water with reference to the main chemical and physical parameters and to the amount of heavy metals (15, 16). In particular, concentrations of toxic components such as Cd, Pb, Hg, and As are very low (<1 μg L^{-1}). This is also confirmed by the analysis of stream sediments, where no anomalous concentration of these elements was detected (10). Concentrations in dissolved components are stable from one year to the other, revealing no changes in water quality from the premining to the postmining period, at least in one year's time.

CONOMA Resolution 20 of the Comissão Nacional de Energia Nuclear, Brazil, represents the environmental reference for uranium (17). This resolution fixes the authorized concentration of U in Brazilian industrial waste discharge at $C_l = 0.4$ Bq L^{-1} (equivalent to 30.8 μg L^{-1} U, about 10 times the mean U concentration in seawater). For comparison, legal limits in the United States and France are respectively 1.1 Bq L^{-1} (84.7 μg L^{-1} U) and 23.4 Bq L^{-1} (1800 μg L^{-1} U). On the basis of Brazilian regulation, three groups of water are distinguished. A first group with very high concentration of U (>200 μg L^{-1}), represented by groundwaters from exploration drillholes (samples 1 and 15) located in gneiss−albitite rocks, is related to the weathering of mineralized bodies. These U concentrations, although higher than the Brazilian limit, represent the natural background in the U-mineralized zone. A second group (samples 4, 6, 15, 18, 19, 21, and 26) including most of the drillholes in gneiss shows U concentrations (10−50 μg L^{-1}) of the same order of magnitude as the Brazilian limit. A third group including excavated wells, streams, ponds, springs, and waters far from the mineralized area exhibits very low U content. No water contamination has been identified outside the area under exploitation.

Leaching Experiments. Though the environmental situation at Lagoa Real appears to be safe, time since the beginning of industrial activity is so short that it cannot be excluded that the waste rocks and the tailings from the processing plant might have a negative impact on the water resources in the future. This induced us to perform some leaching experiments with the aim of characterizing the weathering processes of these materials, focusing on the geochemical behavior of potentially toxic elements. Complete results of the leaching experiments are available in the Supporting Information.

Batch experiments on tailings (LRS1, LRS2, and LRS3) were carried out with deionized water (pH 5.5). The results show that these materials, rinsed with water after the sulfuric acid treatment in the heap leaching and then stored in the dump, still represent a source of many chemical elements, besides U. Among the considered elements, those more easily leached are Al (31 ppm), Fe (26 ppm), and Mn (6.4 ppm), followed by Ba (2.9 ppm), B (2.2 ppm), Sr (1.7 ppm), Zn (1.5
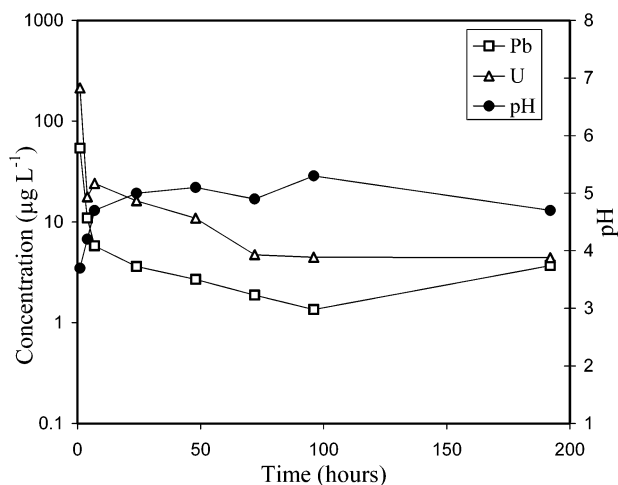

FIGURE 4. Variations in pH, dissolved Pb, and U versus time during the batch experiment on the solid sample LRS3: U-rich ore after sulfuric acid processing.

ppm), U (0.9 ppm), Pb (0.25 ppm), and Rb (0.21 ppm). One group of elements (Mn, Sr, Zn, U, Pb, and Rb) is leached in the first 4 h, when solution pH is 3.8 ± 0.4. Another group (Al, Fe, Ba, and B) shows the maximum dissolution at half experiment, when pH is around 5. The behavior of the first group is probably due to rapid dissolution of secondary sulfate minerals (or other neogenic solid phases). The dissolution of the second group can be explained with slower processes involving aluminum and iron oxihydroxides and not promptly dissoluble aluminum, iron, and barium sulfate minerals. Other elements (Li, V, Tl, Cd, Cu, Co, Ni, and Be) show low extracted contents (<0.1 ppm) and are released in the first hours. Figure 4 shows the variations in pH, Pb, and U versus time for the sample LR3, for which the experiment lasted longer. After 1 h of stirring, pH is acidic (3.5) due to sulfuric acid residues and the highest concentrations of U and Pb are observed. After 4 h, U and Pb decrease significantly and pH rises.

Flow-through reactor experiments were carried out on different solid materials: LRS4 (collected at the same site as LR1, LR2, and LR3) corresponds to tailings derived from the U-rich ore after the H_2SO_4 processing, LRS5 is U-poor ore (i.e., sterile rock), and LRS6 corresponds to U-rich ore before processing. Morphological observations and chemical analysis of the starting materials indicate that plagioclase of oligoclase composition has domains of pure albite. Clinopyroxene and amphiboles have a constant composition, while biotite is often transformed in vermiculite. A low presence of clay minerals was observed.

Experiments on untreated materials (LRS5 and LRS6) lasted 50 days, while experiment on tailings (LRS4) lasted 90 days. In both former experiments, two main stages may be identified: up to 190 h, pH remains relatively high in the

effluent and alkalinity and Na, SO$_4$, and Si concentrations decrease, whereas K and Cl concentrations remain remarkably constant. After 300 h a steady state is reached, where nearly all concentrations remain constant and pH is now close to 6, corresponding to imposed pressure of CO$_2$ (0.05 bar) and alkalinity taken as HCO$_3^-$. The effluent is close to saturation with respect to chalcedony, kaolinite, and calcium clay minerals but constantly undersaturated with respect to uraninite and low-temperature albite. For U this result is in agreement with field observations (saturation with uranophane); regarding albite, dissolution kinetics are probably slow and the flow velocity too high to reach saturation at the experimental conditions. Thermodynamic modeling of the output solution shows that 80% of dissolved U is present as the carbonate complexes (UO$_2$[CO$_3$]$_2^{2-}$ and UO$_2$[CO$_3$]$_3^{4-}$) usually dominant in similar environments (*18*).

The relatively long transition phase could correspond to differences in relative amounts or accessibility of the mineral constituents of rocks. Very dilute chloride and sulfate may here be considered as non-thermodynamically-controlled components and taken as dissolution progress indicators: Cl-bearing minerals seem to enter soon in a steady-state process, whereas some of the SO$_4$-bearing ones selectively disappear. This could correspond to preferential dissolution of the finest, or most altered, material but could also be interpreted as an initial perturbation, like oxidation due to the introduction of oxygen when the experiment is started. In both experiments, solutions are at saturation with fast-dissolving microcrystallized silica (opal-type). In the steady-state phase of the LRS5 experiment, [Ca]/[Mg] $\approx$ 0.8 may correspond to calcite and dolomite codissolution. In LRS6 experiment the nearly constant concentrations of the alkaline earths with [Ca]/[Mg] $\approx$ 0.5 may evidence different dissolving minerals or simply the presence of less-ordered dolomite.

In agreement with results derived from batch experiments, in the LRS4 leachate, pH is initially much more acidic (Figure 5a). Dissolved SO$_4$ is very high (Figure 5b) due to H$_2$SO$_4$ residue: here SO$_4$ is an indicator of the remaining effect of the leaching process in the pile. During the first days of interaction with water, the LRS4 sample releases very high concentrations of U (Figure 5c), as well as Ca, Na, Mg, K, H$_4$SiO$_4$, and Cl, evidencing the presence of highly destabilized minerals. The high silicon value may correspond either to dissolution of amorphous silica or to a contribution of Pyrex corrosion. Dissolution of U is favored by formation of sulfate complexes as long as sulfate remains above the millimolar level. Even after 2000 h, leaching of residual SO$_4$ is not completely eliminated, indicating that rock transformation in the pile-leaching has been important: indeed, with respect to nonprocessed materials (LRS6 experiment), at the end of the present experiment, all measured cations are quite depleted, indicating a fairly insoluble residue, and Cl stabilizes at a much higher value. Uranium is depleted by a factor of 25 with respect to nontreated ore leachate, at the same level as for sterile rock, which evidences the efficiency of the extraction process.

At the end of flow-through reactor experiments, neogenic materials were observed in the columns, brownish-red when derived from untreated ore and yellow-brown from the tailings. Neogenic materials are amorphous (powder X-ray diffraction analysis) and constituted of silicon, aluminum, iron, calcium, and magnesium oxides with about 50% water. The brownish materials were enriched in Fe (30−40%) whereas the yellow product was enriched in Al and Si (50%). On account of their presence, it is reasonable to suppose that iron or aluminum (not measured) might be present in the effluent and balance the observed anions excess. Uranium was not detected in these secondary phases.

Environmental Concerns. The leaching experiments, though not exhaustive, indicate some potential hazards
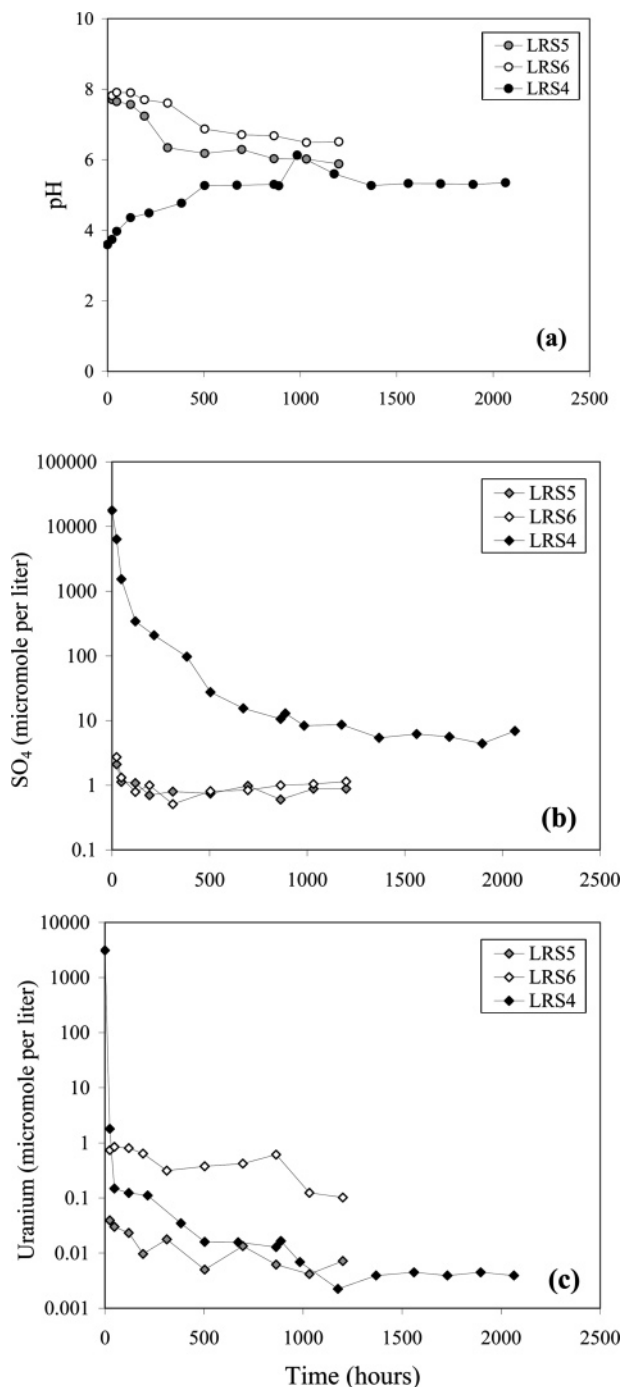

FIGURE 5. Evolution of pH (a), dissolved sulfate (b), and uranium (c) as a function of time during the flow-through reactor experiments on solid samples. LRS4, U-rich ore after sulfuric acid processing; LRS5, waste rock (U-poor material); LRS6, U-rich ore before processing.

connected with the industrial activity. Tailings derived from the ore processing are partially destabilized material due to the H$_2$SO$_4$ attack. The succession of dry and wet periods in a warm climate increases the weathering action of the residual H$_2$SO$_4$. During heavy rainfalls, these materials will potentially acidify the environment and introduce high amounts of sulfate. Furthermore, they might release Ba (possibly with associated radium) and Pb, U, Al, and B in nonnegligible concentrations. This requires that the water from the waste dump is collected, analyzed, and, if necessary, treated before discharge in the environment. Similar processes, but with lower impact, may affect the exposed ore in the open pit. In any case, due to the complexity of the involved processes,

a deeper investigation of the mechanisms of trapping and mobilizing potential contaminants is required.

Accidental scenarios may also be imagined. The leaching pools of the plant may represent another source of contamination in case of breaking of the liner at the bottom. In this case the leak of the leaching liquor, containing U, heavy metals, and H_2SO_4, may originate a local contamination. Something similar could happen in the case of overflow of the leaching liquor due to heavy rain. In both cases it must be assessed that the underlying clay layer acts efficiently as a redundant containment barrier. Contamination may be due also to chemical solvents or extracting agents (organics have not been considered in this study), which may be dangerous by themselves, due to their interaction with the natural environment or as vectors for contaminants.

The present work helps to orient future monitoring of the area. For example, monitoring SO_4 migration seems to be an efficient and simple way to track different hazards: leakage from the tailings (different potential toxic elements) or from the leaching piles (mainly U), accidental acid outflows (due to alteration in clay barriers), or malfunctioning of the U extraction in the plant (multiple contamination).

This study gives only a preexploitation assessment of the environmental risk since the influence of industrial activity was monitored for a short time, and longer monitoring will be needed to measure the impact of both mining and processing. To help further work, a map of the present hazard exposure at Lagoa Real was drawn and published elsewhere (*19*). Georeferenced information, based on a Geographic Information Systems methodology, was combined with the results of the present work. One important feature is the delineation, even in the area around the ore deposit and the treatment plant, of zones of very low present contamination and low degree of expectation of environmental impact by the mining operation. These zones could be taken as reference when looking at any future environmental disturbance.

Acknowledgments

Supporting Information Available

Figures showing a Piper diagram, Na−Cl correlation in groundwaters, and saturation with respect to calcite in drillholes at Lagoa Real and tables with the description and chemical composition of waters and data on field γ-spectrometry and experimental results on solid samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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